
(12) UK Patent Application (19) GB (11) 2 075 517 A

(21) Application No 8113491

(22) Date of filing 1 May 1981

(30) Priority data

(31) 55/057087

(32) 1 May 1980

(33) Japan (JP)

(43) Application published
18 Nov 1981

(51) INT CL³

C08F 8/00 // B32B 27/04
27/28 29/00 C08F 2/38

(52) Domestic classification

C3J CA
B5N 2704 2728 2900
C3P 400 406 420 438
502 GP
C3R 1D1A1 1D2B2 1D2D
1D2E 1E2A 1N2C 1N3 SM
C3W 214
C3Y B230 B240 B245
B262 B263 B270 B284
B286 F581 G200 G300
G310

(56) Documents cited

None

(58) Field of search

C3J

C3P

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(54) Adducts of butadiene type
polymers with phenolic compounds

(57) A process for preparing an adduct
of a butadiene type polymer with a
phenolic compound, comprises (1)
homo- or co-polymerizing butadiene
in the presence of an alkali metal or
organometallic compound thereof as
polymerization initiator and an olefin

as chain transfer agent, and then (2)
reacting the obtained polymer with a
phenolic compound. The product,
which may contain unreacted phenol,
may be further reacted with
formaldehyde.

The modified polymers obtained
may be used as adhesive in laminate
manufacture, e.g. by impregnation
into paper sheets of which a plurality
are then hot-pressed together.

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SPECIFICATION

Process for preparing an adduct of butadiene type polymer with phenolic compound

This invention relates to a process for preparing an excellently soluble adduct of a butadiene type polymer with a phenolic compound and more particularly to a process for preparing such an adduct suitable as starting material for a modified phenolic resin which has excellent electrical properties and will exhibit excellent low-temperature punching workability when punching laminates wherein the resin is used and cured as the adhesive. 5

With the recent technical progress and innovation in the field communication and electronic apparatuses, laminates for use in these apparatuses have come to be required to have very high 10 electrical and physical properties. In addition, such laminates have been required to have excellent punching workability at relatively low temperatures such as ambient temperature from the view-point of the automatization of working equipment, the economization of energy, and the like. 10

In attempts to meet these requirements, there have heretofore been proposed, as adhesives, a phenolic resin incorporated with a thermoplastic polymer, a rubber or a plasticizer, a phenolic resin 15 prepared from a higher alkylphenol derivative, and the like 15

These resins so proposed do not give fully satisfactory results since they disadvantageously provide articles in which they are used as the adhesive, with insufficient flexibility, poor electrical and physical properties, and degraded workability.

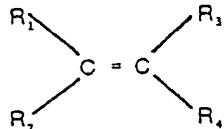
Phenolic resins modified with a drying oil having conjugated double bonds such as tung oil, have 20 relatively little of such disadvantages thereby enabling to give excellent flexibility to articles in which they are used, while they are disadvantageous in that they contain a natural oil which widely varies in price and can no longer satisfy physical and electrical properties required in accordance with the progress of electronic techniques. Thus, a new reactive plasticizer is sought for. 20

There was also proposed a process for preparing a phenolic resin for laminates by reacting a 25 phenolic resin with a drying oil or a liquid polybutadiene in the presence of an acid catalyst and then reacting the resulting reaction product with formaldehyde to produce the phenolic resin. Such a process was proposed in, for example, Japanese Patent Gazette No. 47—43312 and Japanese Patent Laid-Open Gazettes Nos. 48—20890, 48—79895, 49—53628 and 50—109285. 25

On the other hand, phenolic compounds may comparatively easily be addition reacted with a drying 30 oil or liquid diolefin polymer having conjugated double bonds, accompanied by side reactions such as cyclization and polymerization caused at the double bonds portion of the oil or polymer. Thus, if phenolic compounds are attempted to be so addition reacted in a large amount, then the side reactions will remarkably accompany thereby obtaining a high-molecular-weight adduct which will be sparingly soluble in a polar solvent when converted to a varnish, poorly compatible with a phenolic resin and 35 unsatisfactorily permeable to paper or cloths. It will thus be difficult to obtain laminates having good properties if the adduct having these drawbacks is used in the preparation of the laminates. 35

The primary object of this invention is to provide a process for preparing an adduct of a butadiene type polymer with a phenolic compound, the adduct substantially eliminating the above drawbacks.

The process of this invention comprises the steps of (1) polymerizing butadiene alone or 40 copolymerizing butadiene with a vinyl monomer or a diolefin in the presence of an alkali metal or an organometallic compound thereof as the polymerization initiator and in the presence of, as the chain transfer agent, an olefinic compound represented by the following general formula 40



wherein R_1 to R_4 are each hydrogen or an alkyl or aralkyl group having 1 to 20 carbon atoms, to obtain a 45 butadiene type polymer and (2) addition reacting the thus obtained butadiene type polymer with a phenolic compound thereby to obtain an adduct of the butadiene type polymer with the phenolic compound (the adduct being hereinafter referred to as "phenolic compound—addition reacted butadiene type polymer"). 45

The term "butadiene type polymer" used herein is intended to mean a homopolymer of butadiene 50 and a copolymer of butadiene with a vinylic monomer or another diolefin.

According to the present invention, the butadiene type polymer, which is a low-molecular-weight polymer, prepared by the aforementioned specific polymerization method may be addition reacted with a phenolic compound at a high reaction rate in the presence of an acid catalyst to obtain a phenolic compound-addition reacted butadiene type polymer in which the extent of undue increase of the 55 molecular weight is extremely small. It has been found that since such phenolic compound—addition reacted butadiene type polymer contain a relatively large amount of phenolic compound addition reacted and have a molecular weight which is little unduly high, they are excellently soluble in low-boiling polar solvents such as methanol type mixed solvents and acetone solvents and are excellently permeable to paper and cloths. 55

The butadiene type polymers used in this invention include butadiene homopolymers having a number average molecular weight of preferably 200—2000 and butadiene copolymers containing preferably at least 50% of butadiene units. Such butadiene type polymers may be obtained by polymerizing butadiene alone, copolymerizing butadiene with a vinyl monomer having anionically

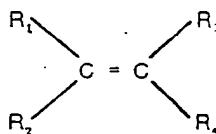
5 polymerizing activity such as styrene or copolymerizing butadiene with a diolefin such as isoprene or 5
piperylene, in the presence of, as the polymerization initiator, an alkali metal (such as lithium or sodium) or an organometallic compound thereof and in the presence of an olefin as the chain transfer agent.

The alkali metals which are a polymerization initiator in this invention include lithium, sodium and 10 potassium metals, and they are usually pulverized or converted to a corresponding organometallic compound prior to their use as a polymerization initiator. The organometallic compounds used herein include butyllithium, benzyllithium, allylsodium, amylsodium, benzylsodium, phenylsodium and amylpotassium. Particularly preferred initiators are an alkylsodium or phenylsodium obtained by reacting an alkyl chloride or phenyl chloride with a sodium dispersion, a benzylsodium type 15 organosodium obtained by the transmetallation reaction of an alkylaryl compound such as toluene, xylene or cumene (Japanese Patent Gazette No. 54—15586) and an allylsodium type organosodium obtained by the transmetallation reaction said alkylsodium or phenylsodium with an olefin such as propylene or butene. The amount of the polymerization initiator usually used herein is in the range of 0.01—1.0 mol per liter of the polymerizing reaction system.

20 The butadiene type polymers according to the invention include homopolymers of butadiene and copolymers of butadiene with the other specific copolymerizable monomer as previously mentioned. The other specific copolymerizable monomers include vinylic monomers having anionically polymerizing activity such as styrene, α -methylstyrene, vinyltoluene and acrylic acid derivatives and also include conjugated dienes other than butadiene, such as isoprene, piperylene 2,3-dimethyl-1,3-butadiene.

25 These comonomers may be used in an amount of up to 50% of butadiene used. 25

The chain transfer agents used in this invention are a hydrocarbon compound which is generally inactive or very slightly active with respect to anionic polymerization, the agents being an olefinic compound represented by the formula



30 wherein R_1 to R_4 are each hydrogen or an alkyl or aralkyl group having 1 to 20 carbon atoms. The chain transfer agents include ethylene, propylene, 1-butene, 2-butene, isobutylene, 2-methyl-2-butene, 2,3-dimethyl-2-butene and 2-hexene. These olefins may be used alone or in combination. The chain transfer agents may be used in an amount of 0.5—150 mol, preferably 3—100 mol, per mol of polymerization initiator used.

35 Solvents for the polymerization may also be used as required in the practice of this invention. They may preferably be a hydrocarbon compound which is inactive with respect to the polymerization and chain transfer reaction. They may preferably be a lower hydrocarbon solvent such as benzene, n-hexane, n-pentane, n-butane or isobutane.

40 Further, a small amount of alcohols, ethers and/or amines may be used as required in the practice of this invention to enhance polymerizing activity and control the molecular weight and microstructure of a butadiene type polymer to be obtained.

The polymerization may be carried out in a wide range of from 180 to 150°C, however, it is preferable to carry out the polymerization at 0—100°C at a reasonable polymerization rate in order to obtain a sparingly colored polymer. The pressure at which the polymerization is effected, is not 45 particularly limited, but it may be atmospheric pressure or a vapor pressure of the reaction system.

The butadiene type polymers used in this invention have a molecular weight of preferably 200—2000, more preferably 300—1000. In the case of such polymers having an unduly low molecular weight, the polymer chain length between the crosslinking points is too small whereby the polymers are inferior in flexibility. If such polymers having an unduly high molecular weight are 50 attempted to be addition reacted with a phenolic compound, the viscosity of the reaction system will increase too much thereby making it possible only to obtain an adduct containing an insufficient amount of the phenolic compound reacted; thus, the adduct so obtained has poor solubility in polar solvents.

When this adduct is attempted to be dissolved in a polar solvent, there will be obtained a solution having a high viscosity and consequently degraded permeability to paper. If said adduct is used in the preparation of laminates, then there will be obtained laminates having lowered electrical properties as well as remarkably degraded resistance to solvents, boiling water and the like.

55 The addition reaction of the butadiene type polymer with the phenolic compound may be effected in the presence, as a catalyst, Bronsted acid such as sulfuric acid, p-toluenesulfonic acid or a sulfonic acid type ion exchange resin, or Lewis acid such as boron trifluoride, boron trifluoride ether complex or aluminum chloride. In brief, the addition reaction in this invention may be effected by a heretofore 60

known method which is applicable to an addition reaction of conventional ordinary butadiene polymers.

As compared with the conventional ordinary butadiene polymers, the butadiene type polymers according to this invention may be addition reacted with the phenolic compound at a high reaction rate while little causing an unduly increase in molecular weight in the resulting adduct, whereby they are addition reacted with a large amount of the phenolic compound. The thus obtained phenolic compound-
5 addition reacted butadiene type polymers are satisfactorily soluble in polar solvents, low in solution viscosity and very excellent in permeation to paper or cloths. Therefore, they may very advantageously be used as material for laminates or the like.

The phenolic compounds used in this invention include phenol, cresol, xylol, resorcine and bisphenol. They may be used alone or in combination.

The amount of the phenolic compounds addition reacted may be in the range of preferably 5—100, more preferably 15—80, parts by weight per 100 parts by weight of the butadiene type polymer.

The addition reaction temperature may be in the range of usually —50 to 200°C, preferably 0 to 15 150°C.

The phenolic compound-addition reacted butadiene type polymers according to this invention may, per se, be cured with hexamethylenetetramine, or they may be blended with a low-molecular-weight phenolic compound-formaldehyde prepolymer and then cured with or without a curing agent such as hexamethylenetetramine.

20 In addition, the phenolic compound-addition reacted butadiene type polymers according to this invention may be incorporated with formaldehyde and, as required, further with a phenolic compound to form a blend which is then reacted in the presence of an acidic or alkaline catalyst to obtain a novolak type or a resol type modified resin.

25 The modified resins so obtained are particularly suitable for use in the preparation of laminates as well as moldings and coating materials. They may be materials for industrial use which have satisfactory 25 flexibility, impact resistance and electrical properties.

This invention will be better understood by the following examples and comparative examples wherein all the parts and percentages are by weight unless otherwise specified.

EXAMPLE 1

30 A sodium dispersion containing 0.88 gram-equivalent was reacted with 0.4 mol of monochlorobenzene to obtain phenylsodium which was incorporated with 1 mol of toluene and then reacted together at 90°C for 5 hours to obtain benzylsodium as an initiator.

The thus obtained benzylsodium was transferred under a nitrogen stream into a 5-liter autoclave, incorporated with 0.3 l of degassed, dehydrated benzene as the solvent and 28 mol of dehydrated 35 isobutylene and then maintained at 40°C. The resulting mixture was incorporated with 20 mol of dehydrated butadiene over a time period of 4.5 hours and then polymerized. After the end of polymerization, methanol was added to the reaction mixture to inactivate the initiator therein and the inactivated initiator was removed.

The solvent, unreacted chain transfer agent and unreacted monomer were removed by distillation, 40 thereby obtaining 1010 g of light-yellow butadiene type polymer. The thus obtained polymer had a viscosity of 64 centipoise at 25°C, a number average molecular weight of 460 and a vinyl bond content of 49%. One hundred (100) grams of this polymer, 138 g of phenol and 1 g of p-toluenesulfonic acid were introduced into a 1-liter flask and then reacted together at 120°C under agitation for 2 hours thereby to obtain an adduct in which 47 g of phenol had been addition reacted with 100 g of the 45 butadiene type polymer. When the thus obtained adduct was attempted to be dissolved in a large amount of acetone, only trace of the insoluble matter was found.

EXAMPLE 2

The procedure for obtaining the butadiene type polymer in Example 1 was followed except that 8 mol of isobutylene was substituted for the 28 mol thereof, to obtain a butadiene type polymer having a 50 viscosity of 200 centipoise at 25°C, a number average molecular weight of 106 and a vinyl bond content of 52%. One hundred (100) grams of this polymer were reacted 138 g of phenol at 120°C for 2 hours in the presence of 1 g of p-toluenesulfonic acid to obtain a butadiene type polymer-phenolic compound adduct in which 43 g of phenol had been addition reacted with 100 g of the butadiene type polymer. This adduct was dissolved in a large amount of acetone with 8% thereof being left insoluble.

55 This insoluble matter was found to be high-molecular-weight polymer by the use of GPC (Gas Permeation Chromatography).

EXAMPLE 3

A sodium dispersion containing 0.88 gram-equivalent was reacted with 0.4 mol of amyl chloride to obtain amylsodium. The thus obtained amylsodium was transferred under a nitrogen stream into a 5-60 liter autoclave, incorporated with 0.3 l of degassed, dehydrated benzene as the solvent and 28 mol of isobutylene and then maintained at 40°C. The resulting mixture was incorporated with 20 mol of dehydrated butadiene over a time period of 4.5 hours thereby to obtain a butadiene type polymer having

a viscosity of 85 centipoise at 25°C, a number average molecular weight of 450 and a vinyl bond content of 49 %.

One hundred (100) grams of the thus obtained butadiene type polymer were reacted with 138 g of phenol at 120°C for 2 hours in the presence of p-toluenesulfonic acid to obtain a phenolic

5 compound—addition reacted butadiene type polymer in which 46 g of phenol had been addition reacted with 100 g of the butadiene type polymer. The thus obtained adduct was dissolved in a large amount of acetone with trace thereof being left insoluble. 5

EXAMPLE 4

Butyllithium (0.051 mol) was charged into a 5-liter autoclave, incorporated with 28 mol of dehydrated isobutylene, maintained at 60°C, incorporated with 20 mol of dehydrated butadiene over a 10 time period of 3 hours and then polymerized thereby to obtain a butadiene type polymer having a viscosity of 80 centipoise at 25°C and a number average molecular weight of 480.

One hundred (100) grams of the thus obtained polymer were reacted with 138 g of phenol at 120°C for 2 hours in the presence of 1 g of p-toluenesulfonic acid to obtain a phenolic compound—addition reacted butadiene type polymer in which 46 g of phenol had been addition reacted with 100 g of the butadiene type polymer. The thus obtained adduct was dissolved in a large amount of acetone with trace thereof being left insoluble. 15

COMPARATIVE EXAMPLE 1

The procedure for obtaining the butadiene type polymer in Example 2 was followed except that 20 toluene was substituted for the chain transfer agent, thereby to obtain a butadiene polymer having a viscosity of 210 centipoise, a number average molecular weight of 650 and a vinyl bond content of 53%.

One hundred (100) grams of the thus obtained butadiene polymer were reacted with 138 g of phenol at 120°C for 2 hours in the presence of 1 g of p-toluenesulfonic acid to obtain a phenolic 25 compound—addition reacted butadiene polymer wherein 36 g of phenol had been addition reacted with 100 g of the butadiene polymer. The thus obtained adduct was dissolved in a large amount of acetone with 15% thereof being left insoluble. The insoluble matter so left was found to be a high-molecular-weight polymer by the use of GPC. 25

COMPARATIVE EXAMPLE 2

30 One hundred (100) grams of 1,4-polybutadiene synthesized using an organonickel catalyst were reacted with 138 g of phenol at 120°C for 2 hours in the presence of 1 g of p-toluenesulfonic acid to obtain a phenolic compound—addition reacted butadiene polymer in which 43 g of phenol had been addition reacted with 100 g of the polybutadiene. The thus obtained adduct was dissolved in a large amount of acetone with 22% thereof being left insoluble. The insoluble matter so left was found to be a 35 high-molecular-weight polymer by the use of GPC. 35

EXAMPLE 5

The whole of the same reaction mixture (including the unreacted phenol) as obtained in Example 1 was incorporated with 143 g of a 37% aqueous solution of formaldehyde and 10 g of a 25% ammonia water to form a mixture which was reacted at 90°C for 30 minutes. The resulting reaction mixture was 40 dehydrated at a reduced pressure (5 mmHg) and incorporated with a toluene-methanol (1:1 by weight) mixed liquid in such an amount as to obtain a varnish having a resin concentration of 50%. 40

The thus obtained varnish was found to have very excellent permeability to kraft paper when it was attempted to be impregnated into the kraft paper. After drying the impregnated varnish, there was obtained resin-impregnated paper having a resin content of 50%.

45 Nine (9) sheets of the thus obtained resin-impregnated paper were put one upon another and then heated to 150°C under a pressure of 100 kg/cm² for 45 minutes thereby obtaining a 1.6 mm thick laminated sheet having the various properties shown in the following Table 1.

EXAMPLE 6

The whole of the same reaction mixture (including the unreacted phenol) as obtained in Example 4 was incorporated with 143 g of a 37% aqueous solution of formaldehyde and 10 g of a 25% ammonia water. The resulting mixture was reacted at 90°C for 30 minutes, dehydrated at a reduced pressure (5 mmHg) and then incorporated with a toluene-methanol (1:1 by weight) mixed liquid in such an amount as to obtain a varnish having a 50% resin content. The thus obtained varnish exhibited excellent permeability to kraft paper when it was impregnated into the paper. Following the procedure of Example 53, a laminated sheet was obtained from sheets of the paper so impregnated. The laminated sheet so obtained had the properties shown in Table 1.

COMPARATIVE EXAMPLE 3

The whole of the same reaction mixture (including the unreacted phenol) as obtained in Comparative Example 1 was incorporated with 143 g of a 37% aqueous solution of formaldehyde and 10 g of a 25% ammonia water to form a mixture which was reacted at 90°C for 30 minutes. The 5 resulting reaction mixture was dehydrated at a reduced pressure (5 mmHg), incorporated with a toluene-methanol (1:1 by weight) mixed liquid in such an amount as to obtain a varnish having a 50% resin content. The thus obtained varnish exhibited unsatisfactory permeability with some amount of the resin remaining on kraft paper when it was attempted to be impregnated into the paper. Following the procedure of Example 3, a laminated sheet was obtained from sheets of the thus resin-impregnated 10 paper. The laminated sheet so obtained has the properties shown in Table 1. 10

COMPARATIVE EXAMPLE 4

The whole of the same reaction mixture (including the unreacted phenol) as obtained in Comparative Example 2 was incorporated with 143 g of a 37% aqueous solution of formaldehyde and 10 g of a 25% ammonia water to form a mixture which was reacted at 90°C for 30 minutes. The 15 resulting reaction mixture was dehydrated at a reduced pressure (5 mmHg) and incorporated with a toluene-methanol (1:1 by weight) mixed liquid in such an amount as to obtain a varnish having a 50% resin content. The thus obtained varnish left some amount of the resin on the surface of kraft paper when it was attempted to be impregnated into the paper. Following the procedure of Example 3, a laminated sheet was obtained from sheets of the resin-impregnated paper so obtained. The thus 20 obtained laminated sheet had the properties shown in Table 1. 20

TABLE 1

| | Example 5 | Example 6 | Comparative Example 3 | Comparative Example 4 |
|---|------------------------|------------------------|--------------------------|------------------------|
| Insulation resistance (Ω) | 8.5×10^{11} | 7.1×10^{11} | 2.0×10^{11} | 5.3×10^{11} |
| | 9.2×10^{10} | 5.5×10^{10} | 7.6×10^6 | 6.6×10^9 |
| Solder heat resistance 260°C (sec.) | 43 | 43 | 5 | 38 |
| Solvent resistance (boiling Trichlore) | 5 minutes Satisfactory | 5 minutes Satisfactory | 5 minutes Unsatisfactory | 5 minutes Satisfactory |
| Punching workability* (ambient temperature) | 90 | 80 | 60 | 80 |

* Tested in accordance with ASTM D617.

As is seen from Table 1, the laminated sheets obtained by using the butadiene type polymer-modified phenolic resins according to this invention as adhesives have not only excellent electrical properties but also excellent punching workability as compared with the comparative ones obtained by using the comparative butadiene polymer-modified phenolic resins as adhesives.

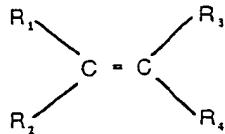
5 EXAMPLE 7

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One hundred (100) parts of the same phenolic compound—addition reacted butadiene type polymer (freed from the unreacted phenol) as obtained in Example 1, 100 parts of novolak type phenol resin, 15 parts of hexamethylenetetramine, 200 parts of wood dust, 4 parts of lime, 4 parts of stearic acid and 4 parts of nigrosine were kneaded together on rolls and then crushed to obtain molding material. A molded article obtained from this molding material had more than twice the impact resistance of a molded article obtained from molding material which was the same in composition except that none of the phenolic compound—addition reacted butadiene type polymer according to this invention was contained. 10

CLAIMS

15 1. A process for preparing a phenolic compound—addition reacted butadiene type polymer, which 15 comprises the steps of
 (1) polymerizing butadiene alone or copolymerizing butadiene with a member selected from the group consisting of vinyl monomers and diolefins in the presence of a member selected from the group consisting of alkali metals and organometallic compounds thereof as the polymerization initiator and in
 20 the presence of, as the chain transfer agent, an olefinic compound represented by the following general 20 formula



wherein R₁ to R₄ are each hydrogen or an alkyl or aralkyl group having 1 to 20 carbon atoms, to obtain a butadiene type polymer and

25 25 2. addition reacting the thus obtained butadiene type polymer with a phenolic compound thereby to obtain the phenolic compound—addition reacted butadiene type polymer.

2. A process according to claim 1, wherein the butadiene type polymer is a butadiene homopolymer having a number average molecular weight of 200—2000 or a butadiene copolymer containing at least 50% of butadiene units.

30 3. A process according to claim 1 or 2, wherein the phenolic compound is at least one member 30 selected from the group consisting of phenol, cresol, xylenol, resorcine and bisphenol.

4. A process according to claim 1, wherein the polymerization initiator is a member selected from the group consisting of lithium, sodium and potassium metals, and butyllithium, benzylolithium, amylsodium, benzylsodium, phenylsodium and amylopotassium.

35 5. A process according to claim 1 or 4, wherein the chain transfer agent is at least one member 35 selected from the group consisting of ethylene, propylene, 1-butene, 2-butene, isobutylene, 2-methyl-2-butene, 2,3-dimethyl-2-butene and 2-hexene.

6. A process according to claim 1 or 2, wherein the vinyl monomer is styrene, α -methylstyrene vinyltoluene or an acrylic acid derivative and the diolefin is isoprene, piperylene, or 2,3-dimethyl-1,3-

40 butadiene. 40

7. A process according to claim 1 or 4, wherein the polymerization initiator is used in an amount of 0.01—1.0 mol per liter of the polymerizing reaction system.

8. A process according to claim 1 or 5, wherein the chain transfer agent is used in an amount of 0.5—150 mol per mol of the polymerization initiator.

45 9. A process according to claim 1, wherein the addition reaction is effected at a temperature from 45 —50 to 200°C.

10. A process according to claim 1, wherein the butadiene type polymer is addition reacted with the phenolic compound in an amount by weight of 5—100 parts per 100 parts of the butadiene type polymer.

50 11. A process for preparing a phenolic compound—addition reacted butadiene type polymer, 50 substantially as described in any one of the foregoing Examples 1 to 7.

12. A phenolic compound—addition reacted butadiene type polymer whenever produced by the process claimed in any one of the preceding claims.